

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 316 541 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.06.2003 Bulletin 2003/23

(51) Int Cl.7: **C07C 45/66, C07C 45/67,
C07C 49/597**

(21) Application number: 02292899.8

(22) Date of filing: 22.11.2002

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 30.11.2001 JP 2001366023

(71) Applicant: **Takasago International Corporation
Tokyo 144-8721 (JP)**

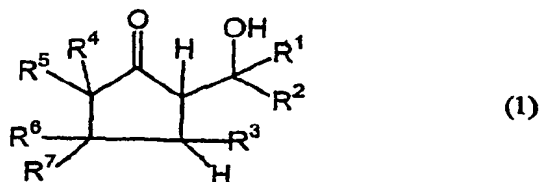
(72) Inventors:
• **Yamamoto, Takeshi,
Takasago International Corp.
Hiratsuka-shi, Kanagawa 254-0073 (JP)**

• **Ujihara, Hideo, Takasago International Corp.
Hiratsuka-shi, Kanagawa 254-0073 (JP)**
• **Adachi, Kenichiro, Takasago International Corp.
Hiratsuka-shi, Kanagawa 254-0073 (JP)**
• **Hagiwara, Toshimitsu,
Takasago International Corp.
Hiratsuka-shi, Kanagawa 254-0073 (JP)**
• **Watanabe, Shinya, Takasago International Corp.
Hiratsuka-shi, Kanagawa 254-0073 (JP)**

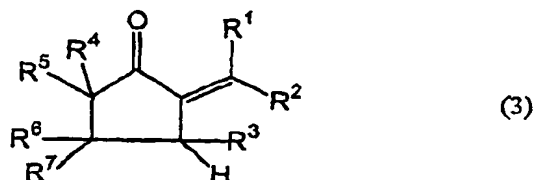
(74) Representative: **Uchida, Kenji et al
S.A. Fedit-Loriot et Autres Conseils en Propriété
Industrielle,
38, avenue Hoche
75008 Paris (FR)**

(54) **Process for producing 2-alkyl-2-cyclopentenones**

(57) Industrially advantageous processes for producing a 2-alkyl-2-cyclopentenone in high yields starting from a 2-(1-hydroxyalkyl)cyclopentanone or a 2-alkylidenecyclopentanone, which are obtainable from a cyclopentanone and a carbonyl compound. A 2-(1-hydroxyalkyl)cyclopentanone represented by the following general formula (1):



is subjected to dehydrative isomerization or a 2-alkylidenecyclopentanone represented by the following general formula (3):



is isomerized. Both reactions take place in the presence of a bromine compound and/or an iodine compound.
In the above formulae, R¹-R⁷ have the meanings given in the description.

Description**FIELD OF THE INVENTION**

[0001] The present invention relates to processes for producing 2-alkyl-2-cyclopentenones useful as industrial products in organic synthetic chemistry, such as medicaments and flavor and fragrance raw materials, and also intermediates thereof.

BACKGROUND OF THE INVENTION

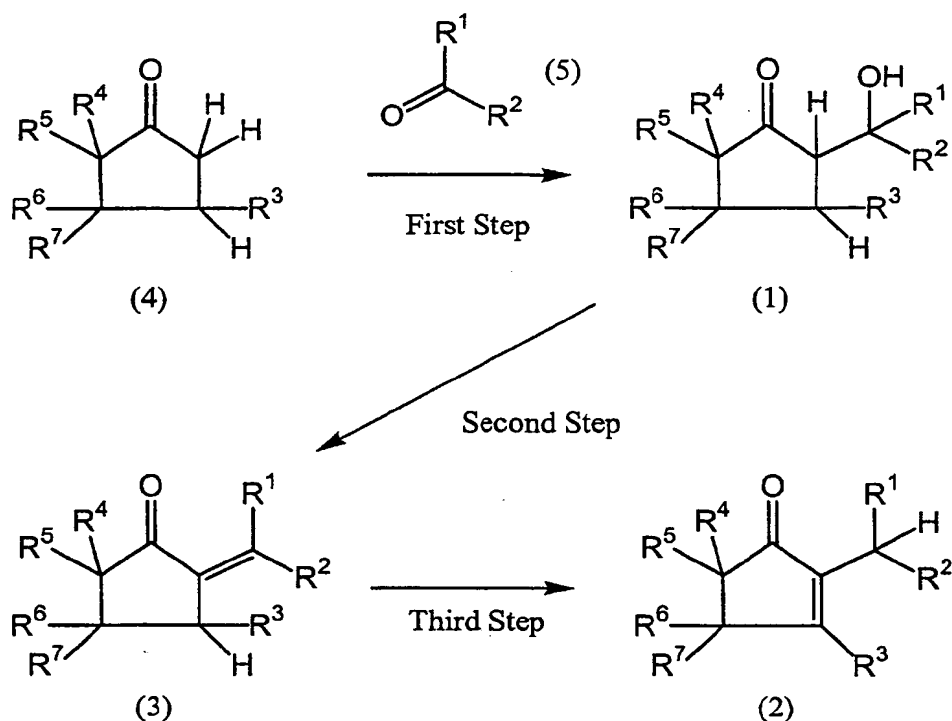
[0002] Heretofore, 2-alkyl-2-cyclopentenones represented by the general formula (2) are known as fruity and floral synthetic fragrance raw materials including jasmine as a representative. In particular, 2-amyl-2-cyclopentenone has a jasmine-like fruity and floral odor and is useful as a fragrance raw material [e.g., Gosei Koryo (Synthetic Flavor and Fragrance Raw Materials)-Kagaku to Shohin Chishiki (Chemistry and Knowledge on Commercial Products)- (written by Motoichi Indo, Kagaku Kogyo Nippo) p. 353].

[0003] Moreover, 2-alkyl-2-cyclopentenones are important as synthetic intermediates. For example, as described in Gosei Koryo (Synthetic Flavor and Fragrance Raw Materials)-Kagaku to Shohin Chishiki (Chemistry and Knowledge on Commercial Products)- (written by Motoichi Indo, Kagaku Kogyo Nippo) pp. 843 - 847, methyl jasmonate and methyl dihydrojasmonate are obtained by adding methyl malonate to 2-cis-pentenyl- and 2-pentyl-2-cyclopentenone and then subjecting the addition products to decarboxylation, respectively. These jasmonates are useful as flavor and fragrance raw materials having a jasmine-like floral odor.

[0004] Furthermore, 2-alkylcyclopentanones obtainable by hydrogenating the double bond of 2-alkyl-2-cyclopentenones are useful as flavor and fragrance raw materials. For example, it is described in Gosei Koryo (Synthetic Flavor and Fragrance Raw Materials)-Kagaku to Shohin Chishiki (Chemistry and Knowledge on Commercial Products)- (written by Motoichi Indo, Kagaku Kogyo Nippo) pp. 353 - 358 that 2-pentylcyclopentanone, 2-hexylcyclopentanone and 2-heptylcyclopentanone are useful as jasmine-like fruity and floral synthetic flavor and fragrance raw materials.

[0005] In addition, δ -lactones obtainable by oxidizing 2-alkylcyclopentanones, for example, using peracetic acid are useful as flavor and fragrance raw materials [Gosei Koryo (Synthetic Flavor and Fragrance Raw Materials)-Kagaku to Shohin Chishiki (Chemistry and Knowledge on Commercial Products)- (written by Motoichi Indo, Kagaku Kogyo Nippo) pp. 562 - 568].

[0006] Heretofore, as a process for producing a 2-alkyl-2-cyclopentenone represented by the formula (2), a process represented by the following reaction scheme (1) has been widely used.



Reaction scheme (1)

[0007] The process involves the following three steps:

First step: a step of obtaining a 2-(1-hydroxyalkyl)cyclopentanone represented by the general formula (1) by treating a cyclopentanone represented by the general formula (4) with an aliphatic carbonyl compound represented by the general formula (5);

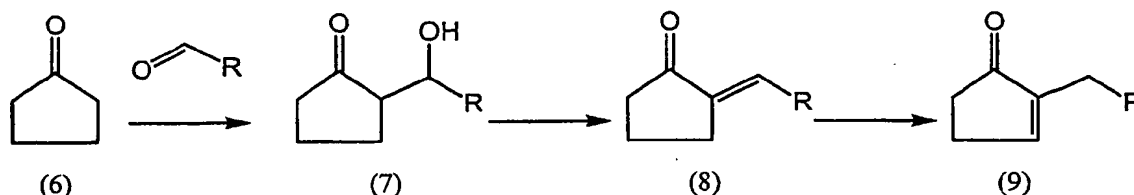
Second step: a step of obtaining a 2-alkylidenecyclopentanone represented by the general formula (3) by dehydrating a 2-(1-hydroxyalkyl)cyclopentanone represented by the general formula (1); and

Third step: a step of producing a 2-alkyl-2-cyclopentenone represented by the general formula (2) by isomerizing a 2-alkylidenecyclopentanone represented by the general formula (3).

[0008] Of these steps, the first step is an application of the reaction, so-called aldol reaction which is well known and, in the case of existing no particular hindrance such as steric hindrance, a 2-(1-hydroxyalkyl)cyclopentanone is obtained in good yields under relatively mild conditions. Moreover, a process is also known wherein a 2-(1-hydroxyalkyl)cyclopentanone, a product in the first step is simultaneously dehydrated to afford a 2-alkylidenecyclopentanone in only one step. In this case, the reaction is particularly called as aldol condensation reaction.

[0009] However, there is room for improvement in the above production of a 2-alkyl-2-cyclopentenone via the above reaction or aldol condensation in view of the yields and operational methods and hence the process is by no means industrially advantageous.

[0010] For example, as shown in the following reaction scheme (2), U.S. Patent No. 4,310,701 discloses a process for obtaining a 2-alkyl-2-cyclopentenone (9) by dehydrating an aldol (7) obtainable from the aldol reaction of cyclopentanone (6) with an aliphatic aldehyde using oxalic acid as a catalyst to afford a 2-alkylidenecyclopentanone (8) and heating it together with an n-butanol solution of concentrated hydrochloric acid to isomerize the double bond.



Reaction scheme (2)

[0011] However, in this process, the yield of the compound (9) calculated based on the compound (6) is not so high and hence the process is not satisfactory. Moreover, some problems, e.g., the inevitable use of a large excess of n-butanol and a large amount of concentrated hydrochloric acid in the isomerization reaction from the compound (8) to the compound (9), are pointed out in view of the production efficiency and thus there is room for improvement as an industrial production process.

[0012] Furthermore, JP-A-5-92934 discloses a process for synthesizing a 2-alkyl-2-cyclopentenone (9) by subjecting the aldol (7) to dehydration and isomerization simultaneously in concentrated hydrochloric acid-n-butanol. However, even in this process, the yield of the compound (9) is not satisfactory and productivity is poor because of the use of a large excess of n-butanol and a large amount of concentrated hydrochloric acid. Thus, for the practical use, there is room for improvement.

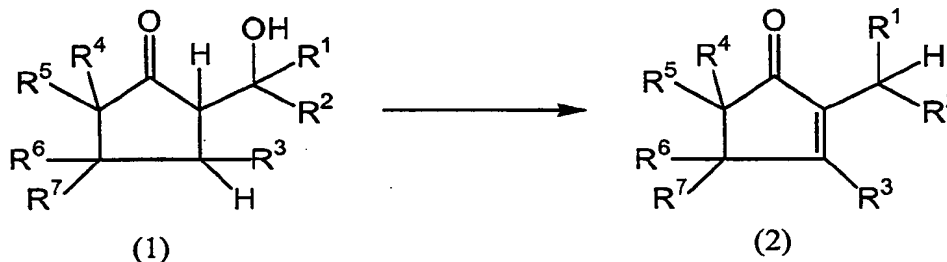
[0013] Additionally, as a catalyst for the reaction of isomerizing the 2-alkylidenecyclopentanone (8) to the 2-alkyl-2-cyclopentenone (9), transition metal complex catalysts are known (JP-B-58-42175 and JP-B-59-29051). However, this process has problems that it produces relatively a large amount of by-products and these catalysts are expensive, so that it is desired to develop an isomerization catalyst which is inexpensive and also excellent in selectivity.

[0014] Moreover, as disclosed in JP-A-2000-327618, JP-A-59-80625 and JP-A-51-23240, isomerization processes using a hydrogen halide or a sulfonic acid are also known. However, in these cases, a large amount of a solvent is used and there is room for improvement of the yield, so that the processes are not industrially advantageous.

SUMMARY OF THE INVENTION

[0015] An object of the invention is to provide industrially advantageous production processes including production of a 2-alkyl-2-cyclopentenone in high yields using a 2-(1-hydroxyalkyl)cyclopentanone or a 2-alkylidenecyclopentanone, which are obtainable from a cyclopentanone and a carbonyl compound.

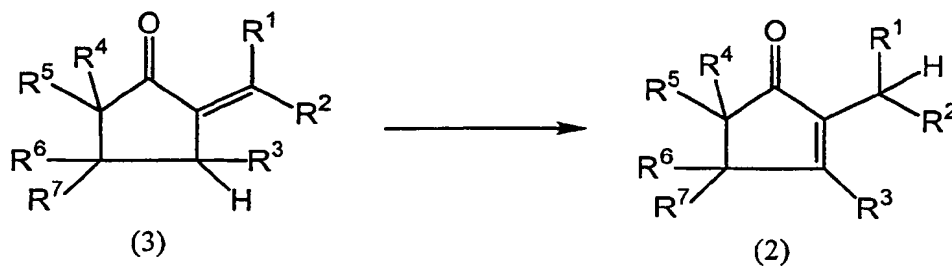
[0016] As a result of intensive studies in consideration of the above circumstances, the present inventors have found that dehydration and isomerization occur simultaneously in high selectivity by reacting a 2-(1-hydroxyalkyl)cyclopentanone represented by the general formula (1) in the presence of a bromine compound and/or an iodine compound as shown in the following reaction scheme (3), and thereby a 2-alkyl-2-cyclopentenone represented by the general formula (2) is obtained in high yields.



Reaction scheme (3)

[0017] Furthermore, as shown in the following reaction scheme (4), they have found that the exocyclic double bond is selectively isomerized to endocyclic double bond by reacting a 2-alkylidenecyclopentanone represented by the following formula (3) in the presence of a catalytic amount of a bromine compound and/or an iodine compound, and

thereby a 2-alkyl-2-cyclopentenone represented by the general formula (2) is obtained in high yields.

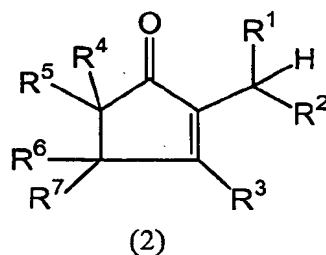


Reaction scheme (4)

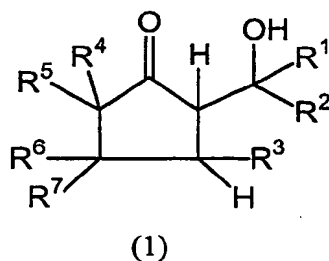
[0018] They have accomplished the invention as a result of further more studies.

[0019] That is, the invention relates to the following.

1) A process for producing a 2-alkyl-2-cyclopentenone represented by the following general formula (2):

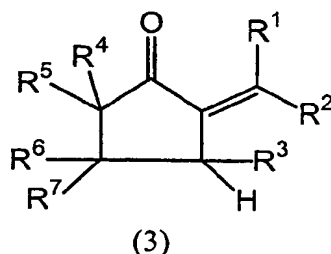


(wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ may be together combined to form a ring which may have a double bond), which comprises a step of dehydrative isomerization of a 2-(1-hydroxyalkyl)cyclopentanone represented by the following general formula (1):



(wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are the same as above) in the presence of a bromine compound and/or an iodine compound.

2) A process for producing a 2-alkyl-2-cyclopentenone represented by the above general formula (2), which comprises a step of isomerization of a 2-alkylidenecyclopentanone represented by the following general formula (3):



(wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are the same as above) in the presence of a bromine compound and/or an iodine compound.

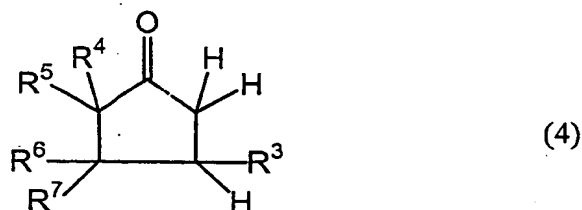
DETAILED DESCRIPTION OF THE INVENTION

[0020] The following will explain the invention in further detail.

[0021] When the phrase "which may have one or more substituents" is used in this specification, the number of the substituents is not particularly limited and is preferably from 1 to 3.

[0022] First, there is explained a process for producing a 2-(1-hydroxyalkyl)cyclopentanone represented by the above general formula (1), which is used in the invention.

[0023] The production process is not particularly limited but, as a representative process, the compound can be produced by applying a well-known aldol reaction starting from a cyclopentanone represented by the following general formula (4)



(wherein R³ to R⁷ are the same as above)
and a carbonyl compound represented by the following general formula (5)



(wherein R¹ and R² are the same as above).

[0024] An aldol reaction is described in Organic Reactions Vol. 16 (John Wiley & Sons INC., 1968), for example.

[0025] In the cyclopentanone represented by the above general formula (4), R³, R⁴, R⁵, R⁶ and R⁷ each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ may be together combined to form a ring which may have a double bond.

[0026] As the substituent by which an alkyl group is substituted, an alkyl group having 1 to 3 carbon atoms may be mentioned, and as the substituent by which an aromatic group is substituted, an alkyl group having 1 to 3 carbon atoms may be mentioned.

[0027] Moreover, the ring which may have a double bond and formed by combining together each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ includes hexahydroindanone, androstane-mono-one, androstene-mono-one, and the like.

[0028] Specific examples of the cyclopentanone represented by the above general formula (4) include cyclopentanone, 2-methylcyclopentanone, 3-methylcyclopentanone, 2-ethylcyclopentanone, 2-propylcyclopentanone, 2-isopropylcyclopentanone, 2-butylcyclopentanone, 2-tert-butylcyclopentanone, 2-iso-butylcyclopentanone, 2-pentylcyclopentanone, 2-hexylcyclopentanone, 2-heptylcyclopentanone, 2-octylcyclopentanone, 2-decylcyclopentanone, 2,2-dimethylcyclopentanone, 2,3-dimethylcyclopentanone, 2,4-dimethylcyclopentanone, and 2,3,4-trimethylcyclopentanone. Among them, preferred is cyclopentanone.

[0029] In the carbonyl compound represented by the above general formula (5), R^1 and R^2 each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and R^1 and R^2 may be together combined to form a ring.

[0030] Specific examples of the carbonyl compound represented by the above general formula (5) include formalin, acetaldehyde, propanal, butanal, pentanal, 3-pentenal, 3-pentynal, hexanal, heptanal, octanal, nonanal, decanal, 2-methylpropanal, 2-methylbutanal, 2-methylpentanal, 2-methylhexanal, 2-methylheptanal, 2-methyloctanal, 3-methylbutanal, 3-methylpentanal, 3-methylhexanal, 4-methylpentanal, 5-methylhexanal, acetone, 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, 2-octanone, 2-nonanone, 4-methyl-2-pentanone, 3-pentanone, cyclopentanone, cyclohexanone and benzaldehyde.

[0031] Among the aliphatic carbonyl compounds represented by the above general formula (5), more preferred are compounds wherein R^1 is hydrogen atom and R^2 is an alkyl group having 1 to 10 carbon atoms which may have any one or more substituents or an aromatic group which may have any one or more substituents.

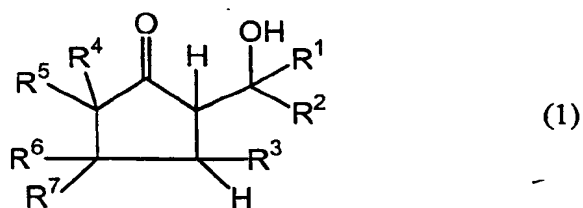
[0032] Specific examples of the compounds include acetaldehyde, propanal, butanal, pentanal, 3-pentenal, 3-pentynal, hexanal, heptanal, octanal, nonanal, decanal, 2-methylpropanal, 2-methylbutanal, 2-methylpentanal, 2-methylhexanal, 2-methylheptanal, 2-methyloctanal, 3-methylbutanal, 3-methylpentanal, 3-methylhexanal, 4-methylpentanal and 5-methylhexanal.

[0033] Further preferred aliphatic carbonyl compound represented by the above general formula (5) are compounds wherein R^1 is hydrogen atom and R^2 is a linear or branched alkyl group having 2 to 8 carbon atoms which may have one or more unsaturated bonds.

[0034] The reaction conditions for the reaction are not particularly limited but aimed 2-(1-hydroxyalkyl)cyclopentanone can be produced easily in high yields, for example, by the reaction using sodium hydroxide as a catalyst.

[0035] In the production of a compound represented by the general formula (2) using a 2-(1-hydroxyalkyl)cyclopentanone represented by the general formula (1) thus obtained, the above reaction product can be used as it is without purification or as a product purified by distillation or the like.

[0036] The following will explain the 2-(1-hydroxyalkyl)cyclopentanone represented by the following general formula (1):



which is used in the invention. In the compound, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R^6 or R^7 with R^3 and (2) R^6 or R^7 with R^4 or R^5 may be together combined to form a ring which may have a double bond.

[0037] Examples of 1-hydroxyalkyl group to be bonded to the 2-position of the above cyclopentanone include hydroxymethyl group, 1-hydroxyethyl group, 1-hydroxypropyl group, 1-hydroxybutyl group, 1-hydroxypentyl group, 1-hydroxy-3-pentenyl group, 1-hydroxy-3-pentynyl group, 1-hydroxyhexyl group, 1-hydroxyheptyl group, 1-hydroxyoctyl group, 1-hydroxynonyl group, 1-hydroxydecyl group, 1-hydroxy-2-methylpropyl group, 1-hydroxy-2-methylbutyl group, 1-hydroxy-2-methylpentyl group, 1-hydroxy-2-methylhexyl group, 1-hydroxy-2-methylheptyl group, 1-hydroxy-2-methyloctyl group, 1-hydroxy-3-methylbutyl group, 1-hydroxy-3-methylpentyl group, 1-hydroxy-3-methylhexyl group, 1-hydroxy-4-methylpentyl group, 1-hydroxy-5-methylhexyl group, 1-hydroxy-1-methylethyl group, 1-hydroxy-1-methylpropyl group, 1-hydroxy-1-methylbutyl group, 1-hydroxy-1-methylpentyl group, 1-hydroxy-1-methylhexyl group, 1-hydroxy-1-methylheptyl group, 1-hydroxy-1-methyloctyl group, 1-hydroxy-1,3-dimethylbutyl group, 1-hydroxy-1-ethylpropyl group, 1-hydroxycyclopentyl group, 1-hydroxycyclohexyl group and hydroxyphenylmethyl group.

[0038] Moreover, as cyclopentanones substituted at the 2-position, there may be mentioned those wherein the fol-

lowing cyclopentanones are substituted by any of the above 1-hydroxyalkyl group at the 2-position. Specific examples of the cyclopentanones to be substituted by the above 1-hydroxyalkyl group include cyclopentanone, 5-methylcyclopentanone, 3- or 4-methylcyclopentanone, 5-ethylcyclopentanone, 5-propylcyclopentanone, 5-isopropylcyclopentanone, 5-butylcyclopentanone, 5-tert-butylcyclopentanone, 5-iso-butylcyclopentanone, 5-pentylcyclopentanone, 5-hexylcyclopentanone, 5-heptylcyclopentanone, 5-octylcyclopentanone, 5-decylcyclopentanone, 5,5-dimethylcyclopentanone, 4,5-dimethylcyclopentanone, 3,5-dimethylcyclopentanone, and 3,4,5-trimethylcyclopentanone.

[0039] Among the cyclopentanones substituted at the 2-position, preferred are compounds wherein R^1 is hydrogen atom, R^2 , R^3 , R^4 , R^5 , R^6 and R^7 each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R^6 or R^7 with R^3 and (2) R^6 or R^7 with R^4 or R^5 may be together combined to form a ring which may have a double bond.

[0040] More specifically, examples of 1-hydroxyalkyl group to be bonded to the cyclopentanones include hydroxymethyl group, 1-hydroxyethyl group, 1-hydroxypropyl group, 1-hydroxybutyl group, 1-hydroxypentyl group, 1-hydroxy-3-pentenyl group, 1-hydroxy-3-pentynyl group, 1-hydroxyhexyl group, 1-hydroxyheptyl group, 1-hydroxyoctyl group, 1-hydroxynonyl group, 1-hydroxydecyl group, 1-hydroxy-2-methylpropyl group, 1-hydroxy-2-methylbutyl group, 1-hydroxy-2-methylpentyl group, 1-hydroxy-2-methylhexyl group, 1-hydroxy-2-methyloctyl group, 1-hydroxy-3-methylbutyl group, 1-hydroxy-3-methylpentyl group, 1-hydroxy-3-methylhexyl group, 1-hydroxy-4-methylpentyl group and 1-hydroxy-5-methylhexyl group.

[0041] Moreover, as cyclopentanones substituted at the 2-position, there may be mentioned those wherein the following cyclopentanones are substituted by any of the above 1-hydroxyalkyl group at the 2-position. Specific examples of the cyclopentanones to be substituted by the above 1-hydroxyalkyl group include cyclopentanone, 5-methylcyclopentanone, 3- or 4-methylcyclopentanone, 5-ethylcyclopentanone, 5-propylcyclopentanone, 5-isopropylcyclopentanone, 5-butylcyclopentanone, 5-tert-butylcyclopentanone, 5-iso-butylcyclopentanone, 5-pentylcyclopentanone, 5-hexylcyclopentanone, 5-heptylcyclopentanone, 5-octylcyclopentanone, 5-decylcyclopentanone, 5,5-dimethylcyclopentanone, 4,5-dimethylcyclopentanone, 3,5-dimethylcyclopentanone, and 3,4,5-trimethylcyclopentanone.

[0042] Among the cyclopentanones substituted at the 2-position, more preferred are compounds wherein R^2 is an alkyl group having 1 to 10 carbon atoms which may have any one or more substituents or an aromatic group which may have any one or more substituents, and R^1 , R^3 , R^4 , R^5 , R^6 and R^7 each is hydrogen atom.

[0043] Specific examples of the preferred compounds include 2-(1-hydroxyethyl)cyclopentanone, 2-(1-hydroxypropyl)cyclopentanone, 2-(1-hydroxybutyl)cyclopentanone, 2-(1-hydroxypentyl)cyclopentanone, 2-(1-hydroxy-3-pentenyl)cyclopentanone, 2-(1-hydroxy-3-pentynyl)cyclopentanone, 2-(1-hydroxyhexyl)cyclopentanone, 2-(1-hydroxyoctyl)cyclopentanone, 2-(1-hydroxynonyl)cyclopentanone, 2-(1-hydroxydecyl)cyclopentanone, 2-(1-hydroxy-2-methylpropyl)cyclopentanone, 2-(1-hydroxy-2-methylbutyl)cyclopentanone, 2-(1-hydroxy-2-methylpentyl)cyclopentanone, 2-(1-hydroxy-2-methylhexyl)cyclopentanone, 2-(1-hydroxy-2-methylheptyl)cyclopentanone, 2-(1-hydroxy-2-methyloctyl)cyclopentanone, 2-(1-hydroxy-3-methylbutyl)cyclopentanone, 2-(1-hydroxy-3-methylpentyl)cyclopentanone, 2-(1-hydroxy-3-methylhexyl)cyclopentanone, 2-(1-hydroxy-4-methylpentyl)cyclopentanone and 2-(1-hydroxy-5-methylhexyl)cyclopentanone.

[0044] More preferred are compounds wherein R^2 is a linear or branched alkyl group having 2 to 8 carbon atoms which may have one or more unsaturated bonds, and R^1 , R^3 , R^4 , R^5 , R^6 and R^7 each is hydrogen atom.

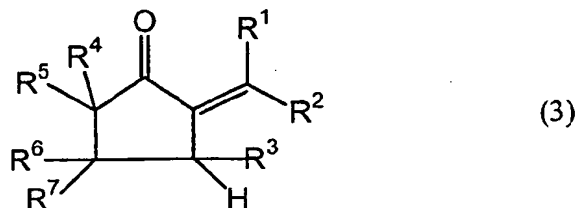
[0045] Specific examples of the compounds include 2-(1-hydroxypropyl)cyclopentanone, 2-(1-hydroxybutyl)cyclopentanone, 2-(1-hydroxypentyl)cyclopentanone, 2-(1-hydroxy-3-pentenyl)cyclopentanone, 2-(1-hydroxy-3-pentynyl)cyclopentanone, 2-(1-hydroxyhexyl)cyclopentanone, 2-(1-hydroxyheptyl)cyclopentanone, 2-(1-hydroxyoctyl)cyclopentanone, 2-(1-hydroxy-2-methylpropyl)cyclopentanone, 2-(1-hydroxy-2-methylbutyl)cyclopentanone, 2-(1-hydroxy-2-methylpentyl)cyclopentanone, 2-(1-hydroxy-2-methylhexyl)cyclopentanone, 2-(1-hydroxy-3-methylbutyl)cyclopentanone, 2-(1-hydroxy-3-methylpentyl)cyclopentanone, 2-(1-hydroxy-3-methylhexyl)cyclopentanone, 2-(1-hydroxy-4-methylpentyl)cyclopentanone and 2-(1-hydroxy-5-methylhexyl)cyclopentanone.

[0046] In the invention, a process for producing a 2-alkylidenecyclopentanone represented by the general formula (3) which is another starting material is also not particularly limited, but as a representative process, there may be mentioned a process for producing the compound via an aldol condensation well known to those skilled in the art starting from a cyclopentanone represented by the general formula (4) and an aliphatic carbonyl compound represented by the general formula (5), for example.

[0047] Specifically, for example, an aimed 2-alkylidenecyclopentanone can be also produced by reacting a cyclopentanone represented by the general formula (4) with an aliphatic carbonyl compound represented by the general formula (5) in the presence of sodium hydroxide as a catalyst to produce a 2-(1-hydroxyalkyl)cyclopentanone and, after isolation of the product, subjecting it to dehydration. On the other hand, an aimed 2-alkylidenecyclopropanone can be directly produced by reacting a cyclopentanone represented by the general formula (4) with an aliphatic carbonyl compound represented by the general formula (5) in the presence of sodium hydroxide as a catalyst without isolation of a 2-(1-hydroxyalkyl)cyclopentanone.

[0048] At the use of a 2-alkylidenecyclopentanone thus obtained as a starting material of the invention, the reaction product can be used as it is without purification or as a product purified by distillation or the like.

[0049] In the 2-alkylidenecyclopentanone represented by the following general formula (3):



R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ may be together combined to form a ring which may have a double bond.

[0050] The alkylidene group by which the above compound is substituted at the 2-position is selected from the group consisting of methylidene group, ethylidene group, propylidene group, butylidene group, pentylidene group, hexylidene group, heptylidene group, octylidene group, nonylidene group, decylidene group, 2-methylpropylidene group, 2-methylbutylidene group, 2-methylpentylidene group, 2-methylhexylidene group, 2-methyloctylidene group, 3-methylbutylidene group, 3-methylpentylidene group, 3-methylhexylidene group, 4-methylpentylidene group, 5-methylhexylidene group, 1-methylethylidene group, 1-methylpropylidene group, 1-methylbutylidene group, 1-methylpentylidene group, 1-methylhexylidene group, 1-methylheptylidene group, 1-methyloctylidene group, 1,3-dimethylbutylidene group, 1-ethylpropylidene group, and benzylidene group.

[0051] As cyclopentanones substituted at the 2-position, there may be mentioned those wherein the following cyclopentanones are substituted by any of the above alkylidene group at the 2-position. Specific examples of the cyclopentanones to be substituted include cyclopentanone, 5-methylcyclopentanone, 3- or 4-methylcyclopentanone, 5-ethylcyclopentanone, 5-propylcyclopentanone, 5-isopropylcyclopentanone, 5-butylcyclopentanone, 5-tert-butylcyclopentanone, 5-iso-butylcyclopentanone, 5-pentylcyclopentanone, 5-hexylcyclopentanone, 5-heptylcyclopentanone, 5-octylcyclopentanone, 5-decylcyclopentanone, 5,5-dimethylcyclopentanone, 4,5-dimethylcyclopentanone, 3,5-dimethylcyclopentanone, and 3,4,5-trimethylcyclopentanone.

[0052] Among cyclopentanones substituted at the 2-position, more preferred are compounds wherein R¹ is hydrogen atom, R², R³, R⁴, R⁵, R⁶ and R⁷ each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ may be together combined to form a ring which may have a double bond.

[0053] Specifically, examples of the alkylidene group bonded to the cyclopentanones at the 2-position include methylidene group, ethylidene group, propylidene group, butylidene group, pentylidene group, hexylidene group, heptylidene group, octylidene group, nonylidene group, decylidene group, 2-methylpropylidene group, 2-methylbutylidene group, 2-methylpentylidene group, 2-methylhexylidene group, 2-methylheptylidene group, 2-methyloctylidene group, 3-methylbutylidene group, 3-methylpentylidene group, 3-methylhexylidene group, 4-methylpentylidene group and 5-methylhexylidene group.

[0054] As cyclopentanones substituted at the 2-position, there may be mentioned those wherein the following cyclopentanones are substituted by any of the above alkylidene group at the 2-position. Specific examples of the cyclopentanones to be substituted include cyclopentanone, 5-methylcyclopentanone, 3- or 4-methylcyclopentanone, 5-ethylcyclopentanone, 5-propylcyclopentanone, 5-isopropylcyclopentanone, 5-butylcyclopentanone, 5-tert-butylcyclopentanone, 5-iso-butylcyclopentanone, 5-pentylcyclopentanone, 5-hexylcyclopentanone, 5-heptylcyclopentanone, 5-octylcyclopentanone, 5-decylcyclopentanone, 5,5-dimethylcyclopentanone, 4,5-dimethylcyclopentanone, 3,5-dimethylcyclopentanone, and 3,4,5-trimethylcyclopentanone.

[0055] More preferred are compounds wherein R² is an alkyl group having 1 to 10 carbon atoms which may have any one or more substituents or an aromatic group which may have any one or more substituents, and R¹, R³, R⁴, R⁵, R⁶ and R⁷ each is hydrogen atom.

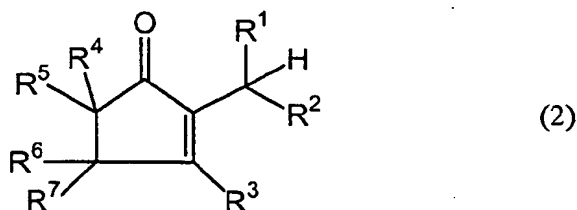
[0056] Specific examples of the compounds include 2-ethylidenecyclopentanone, 2-propylidenecyclopentanone, 2-butylidenecyclopentanone, 2-pentylidenecyclopentanone, 2-hexylidenecyclopentanone, 2-heptylidenecyclopentanone, 2-octylidenecyclopentanone, 2-nonylidenecyclopentanone, 2-decylidenecyclopentanone, 2-(2-methylpropylidene)cyclopentanone, 2-(2-methylbutylidene)cyclopentanone, 2-(2-methylpentylidene)cyclopentanone, 2-(2-methyl-

hexylidene)cyclopentanone, 2-(2-methyloctylidene)cyclopentanone, 2-(3-methylbutylidene)cyclopentanone, 2-(3-methylpentylidene)cyclopentanone, 2-(3-methylhexylidene)cyclopentanone, 2-(4-methylpentylidene)cyclopentanone and 2-(5-methylhexylidene)cyclopentanone.

[0057] Particularly preferred are compounds wherein R² is a linear or branched alkyl group having 2 to 8 carbon atoms which may have one or more unsaturated bonds, and R¹, R³, R⁴, R⁵, R⁶ and R⁷ each is hydrogen atom.

[0058] Specific examples of the compounds include 2-propylidenecyclopentanone, 2-butylidenecyclopentanone, 2-pentylidenecyclopentanone, 2-hexylidenecyclopentanone, 2-heptylidenecyclopentanone, 2-octylidenecyclopentanone, 2-(2-methylpropylidene)cyclopentanone, 2-(2-methylbutylidene)cyclopentanone, 2-(2-methylpentylidene)cyclopentanone, 2-(2-methylhexylidene)cyclopentanone, 2-(3-methylbutylidene)cyclopentanone, 2-(3-methylpentylidene)cyclopentanone, 2-(3-methylhexylidene)cyclopentanone, 2-(4-methylpentylidene)cyclopentanone and 2-(5-methylhexylidene)cyclopentanone.

[0059] The 2-alkyl-2-cyclopentenone represented by the following general formula (2):



which is an aimed compound of the invention is a compound wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have any one or more substituents or an aromatic group which may have any one or more substituents, and each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ may be together combined to form a ring which may have a double bond).

[0060] In the above compound (2), examples of the alkyl group bonded to the 2-cyclopentenone at the 2-position include methyl group, ethyl group, propyl group, butyl group, pentyl group, 3-pentenyl group, 3-pentynyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, 2-methylpropyl group, 2-methylbutyl group, 2-methylpentyl group, 2-methylhexyl group, 2-methyloctyl group, 3-methylbutyl group, 3-methylpentyl group, 3-methylhexyl group, 4-methylpentyl group, 5-methylhexyl group, 1-methylethyl group, 1-methylpropyl group, 1-methylbutyl group, 1-methylpentyl group, 1-methylhexyl group, 1-methylheptyl group, 1-methyloctyl group, 1,3-dimethylbutyl group, 1-ethylpropyl group, and phenylmethyl group.

[0061] As cyclopentanones substituted at the 2-position, there may be mentioned those wherein the following cyclopentanones are substituted by any of the above alkyl group at the 2-position. Specific examples of the 2-cyclopentanones to be substituted include 2-cyclopentenone, 5-methyl-2-cyclopentenone, 3- or 4-methyl-2-cyclopentenone, 5-ethyl-2-cyclopentenone, 5-propyl-2-cyclopentenone, 5-isopropyl-2-cyclopentenone, 5-butyl-2-cyclopentenone, 5-tert-butyl-2-cyclopentenone, 5-iso-butyl-2-cyclopentenone, 5-pentyl-2-cyclopentenone, 5-hexyl-2-cyclopentenone, 5-heptyl-2-cyclopentenone, 5-octyl-2-cyclopentenone, 5-decyl-2-cyclopentenone, 5,5-dimethyl-2-cyclopentenone, 4,5-dimethyl-2-cyclopentenone, 3,5-dimethyl-2-cyclopentenone, and 3,4,5-trimethyl-2-cyclopentenone.

[0062] Preferred are compound wherein R¹ is hydrogen atom, R², R³, R⁴, R⁵, R⁶ and R⁷ each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ may be together combined to form a ring which may have a double bond.

[0063] In the above compound, examples of the alkyl group bonded to the 2-cyclopentenone at the 2-position include methyl group, ethyl group, propyl group, butyl group, pentyl group, 3-pentenyl group, 3-pentynyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, 2-methylpropyl group, 2-methylbutyl group, 2-methylpentyl group, 2-methylhexyl group, 2-methyloctyl group, 3-methylbutyl group, 3-methylpentyl group, 3-methylhexyl group, 4-methylpentyl group and 5-methylhexyl group.

[0064] As 2-cyclopentanones substituted at the 2-position, there may be mentioned those wherein the following cyclopentanones are substituted by any of the above alkyl group at the 2-position. Specific examples of the 2-cyclopentanones to be substituted include 2-cyclopentenone, 5-methyl-2-cyclopentenone, 3- or 4-methyl-2-cyclopentenone, 5-ethyl-2-cyclopentenone, 5-propyl-2-cyclopentenone, 5-isopropyl-2-cyclopentenone, 5-butyl-2-cyclopentenone, 5-tert-butyl-2-cyclopentenone, 5-iso-butyl-2-cyclopentenone, 5-pentyl-2-cyclopentenone, 5-hexyl-2-cyclopentenone, 5-heptyl-2-cyclopentenone, 5-octyl-2-cyclopentenone, 5-decyl-2-cyclopentenone, 5,5-dimethyl-2-cyclopentenone, 4,5-dimethyl-2-cyclopentenone, 3,5-dimethyl-2-cyclopentenone, and 3,4,5-trimethyl-2-cyclopentenone.

[0065] More preferred are compounds wherein R² is an alkyl group having 1 to 10 carbon atoms which may have

any one or more substituents or an aromatic group which may have any one or more substituents, and R¹, R³, R⁴, R⁵, R⁶ and R⁷ each is hydrogen atom.

• **[0066]** Specific examples of the compounds include 2-ethyl-2-cyclopentenone, 2-propyl-2-cyclopentenone, 2-butyl-2-cyclopentenone, 2-pentyl-2-cyclopentenone, 2-(3-pentenyl)-2-cyclopentenone, 2-(3-pentynyl)-2-cyclopentenone, 2-hexyl-2-cyclopentenone, 2-heptyl-2-cyclopentenone, 2-octyl-2-cyclopentenone, 2-nonyl-2-cyclopentenone, 2-decyl-2-cyclopentenone, 2-(2-methylpropyl)-2-cyclopentenone, 2-(2-methylbutyl)-2-cyclopentenone, 2-(2-methylpentyl)-2-cyclopentenone, 2-(2-methylhexyl)-2-cyclopentenone, 2-(2-methyloctyl)-2-cyclopentenone, 2-(3-methylbutyl)-2-cyclopentenone, 2-(3-methylpentyl)-2-cyclopentenone, 2-(3-methylhexyl)-2-cyclopentenone, 2-(4-methylpentyl)-2-cyclopentenone and 2-(5-methylhexyl)-2-cyclopentenone.

[0067] Particularly preferred are compounds wherein R² is a linear or branched alkyl group having 2 to 8 carbon atoms which may have one or more unsaturated bonds, and R¹, R³, R⁴, R⁵, R⁶ and R⁷ each is hydrogen atom.

[0068] Specific examples of the compounds include 2-propyl-2-cyclopentenone, 2-butyl-2-cyclopentenone, 2-pentyl-2-cyclopentenone, 2-(3-pentenyl)-2-cyclopentenone, 2-(3-pentynyl)-2-cyclopentenone, 2-hexyl-2-cyclopentenone, 2-heptyl-2-cyclopentenone, 2-octyl-2-cyclopentenone, 2-(2-methylbutyl)-2-cyclopentenone, 2-(2-methylpentyl)-2-cyclopentenone, 2-(2-methylhexyl)-2-cyclopentenone, 2-(3-methylbutyl)-2-cyclopentenone, 2-(3-methylpentyl)-2-cyclopentenone, 2-(3-methylhexyl)-2-cyclopentenone, 2-(4-methylpentyl)-2-cyclopentenone and 2-(5-methylhexyl)-2-cyclopentenone.

[0069] One characteristic of the invention is that, in the reaction of forming a 2-alkyl-2-cyclopentenone represented by the general formula (2) by dehydration followed by isomerization of a 2-(1-hydroxyalkyl)cyclopentanone represented by the general formula (1) or by isomerization of 2-alkylidenecyclopentanone represented by the general formula (3), a bromine compound and/or an iodine compound are employed and made present in the reaction system.

[0070] The bromine compound to be used in the invention means a compound which forms bromine in the reaction system under the conditions used in the invention and the iodine compound means a compound which forms iodine in the reaction system under the conditions used in the invention. Furthermore, the bromine compound includes bromine itself and the above iodine compound includes iodine itself.

[0071] Thus, the invention also involves, in addition to a method of adding bromine and/or iodine, a method of forming bromine and/or iodine in the reaction system and a method of forming an active species having ability almost equal to that of the active species formed at the time when bromine and/or iodine are added to the reaction system, by adding a bromine compound and/or an iodine compound to the reaction system.

[0072] The method of forming bromine and/or iodine in the reaction system and a method of forming an active species almost equal to the active species formed at the time when bromine and/or iodine are added to the reaction system are not particularly limited but the following may be exemplified:

- 1) hydrohalogenic acids containing bromine ion and/or iodine ion, and salts thereof,
- 2) organic compounds having carbon-bromine bond and/or carbon-iodine bond,
- 3) organic compounds having silicon-bromine bond and/or silicon-iodine bond,
- 4) organic compounds having nitrogen-bromine bond and/or nitrogen-iodine bond,
- 5) compounds having bond(s) between boron, phosphorus or sulfur and bromine and/or iodine, and
- 6) metal complex compounds containing bromine and/or iodine. These compounds are oxidized with an oxidizing agent such as oxygen in the air or reacted with a reaction substrate or solvent to form bromine and/or iodine.

[0073] Preferably, bromine and iodine are mentioned as specific examples but the invention is not limited thereto.

[0074] When illustrated on the basis of the reaction starting material, the amount of the above bromine compound and/or iodine compound to be used is preferably from 0.0001 to 2.0% by weight, more preferably from 0.01 to 0.5% by weight in terms of bromine and/or iodine. The larger amount of the compounds results in the faster reaction rate, but is economically disadvantageous.

[0075] The reaction temperature varies depending on the bromine compound and/or iodine compound, but generally ranges from 70 to 220°C, preferably from 100 to 170°C.

[0076] Moreover, the reaction may proceed without any solvent but it is preferred to use an appropriate amount of a solvent. As the solvent, use can be made of hydrocarbons such as toluene, xylene, decaline, tetraline, hexane, heptane, n-octane, isooctane, cyclooctane and cyclododecane, halogenated hydrocarbons such as tetrachloroethane, tetrachloroethylene and ketones such as cyclopentanone.

[0077] The amount thereof varies depending on the solvent to be used and hence is not particularly limited, but it is common to control the ratio of the volume (ml) of the solvent to the weight (g) of the reaction starting material to be 1/5 to 5/1.

[0078] According to the invention, it is enabled to produce a 2-alkyl-2-cyclopentenone represented by the general formula (2) in one step and easily in high yields. Namely, a 2-alkyl-2-cyclopentenone can be produced in one step and easily in high yields by facile operation that a bromine compound and/or an iodine compound is added to a reaction

EP 1 316 541 A1

system containing a 2-(1-hydroxyalkyl)cyclopentanone represented by the general formula (1).

[0079] The following will explain the invention with reference to Examples but the invention is by no means limited thereto.

[0080] Incidentally, the instruments employed for measuring the physical properties in Examples are as follows.

Chemical Purity

[0081]

Gas chromatograph: HP-6890 (Hewlett-Packard)
Column: HP-5 (30 m x 0.25 mm x 0.25 mm)

Nuclear Magnetic Resonance

[0082]

¹H-NMR: Bruker-AMX400 (400 MHz) (Bruker)

Mass Spectrometry (GC-MS)

[0083]

HP-6890 (Hewlett-Packard)
Column: HP-1 (60 m x 0.25 mm x 0.25 mm)

Reference Example 1

Synthesis of 2-(1-hydroxypentyl)cyclopentanone

[0084] Into a 2-liter four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were added sodium hydroxide (3.2 g) and water (300 ml). Then, a mixture of pentanal (86 g) and cyclopentanone (152 g) was added dropwise with stirring at 0 - 5°C over a period of 2 hours. After the addition, the reaction mixture was stirred at room temperature for 1 hour to complete the reaction. Hexane (150 ml) was added to the reaction mixture and the layers were separated from each other. The resulting organic layer was washed with an aqueous solution (200 ml) of acetic acid (1 g) and then separated. The resulting organic layer was washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover hexane and unreacted cyclopentanone, whereby a crude product (173 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 127 g of 2-(1-hydroxypentyl)cyclopentanone (boiling point: 115°C/933 Pa; GC purity: 95%). The remaining 5% was 2-pentylidenecyclopentanone which is a dehydration product.

Reference Example 2

Synthesis of 2-(1-hydroxyhexyl)cyclopentanone

[0085] Into a 2-liter four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were added sodium hydroxide (3.2 g) and water (300 ml). Then, a mixture of hexanal (100 g) and cyclopentanone (152 g) was added dropwise thereto under stirring at 0 - 5°C over a period of 2 hours. After the addition, the reaction mixture was stirred at room temperature for 1 hour to complete the reaction. Hexane (150 ml) was added to the reaction mixture and the layers were separated from each other. The resulting organic layer was washed with an aqueous solution (200 ml) of acetic acid (1 g) and then separated. The resulting organic layer was further washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover hexane and unreacted cyclopentanone, whereby a crude product (188 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 142 g of 2-(1-hydroxyhexyl)cyclopentanone (boiling point: 107 - 108°C/666 Pa; GC purity: 94%). The remaining 6% was 2-hexylidenecyclopentanone which is a dehydration product.

Reference Example 3

• Synthesis of 2-(1-hydroxyheptyl)cyclopentanone

5 **[0086]** Into a 2-liter four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were added sodium hydroxide (3.2 g) and water (300 ml). Then, a mixture of heptanal (114 g) and cyclopentanone (152 g) was added dropwise thereto under stirring at 0 - 5°C over a period of 2 hours. After the addition, the reaction mixture was stirred at room temperature for 1 hour to complete the reaction. Hexane (150 ml) was added to the reaction mixture and the layers were separated from each other. The resulting organic layer was washed with an aqueous solution (200 ml) of acetic acid (1 g) and separated. Then, the resulting organic layer was washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover hexane and unreacted cyclopentanone, whereby a product (202 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 154 g of 2-(1-hydroxyheptyl)cyclopentanone (boiling point: 112 - 114°C/666 Pa; GC purity: 92%). The remaining 8% was 2-heptylidenecyclopentanone which is a dehydration product.

Reference Example 4

Synthesis of 2-pentylidenecyclopentanone

20 **[0087]** In a 300 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-(1-hydroxyheptyl)cyclopentanone (70 g) synthesized in Reference Example 1, oxalic acid (0.7 g) and toluene (140 ml), and the whole was refluxed to allow dehydration to proceed. The formed water was removed and the reaction was continued until water was not formed any more (about 2.5 hours). The reaction mixture was washed with water and the layers were separated from each other. The resulting organic layer was further washed with saturated brine and separated. 25 The organic layer was evaporated on a rotary evaporator under reduced pressure to recover toluene and unreacted cyclopentanone, whereby a crude product (63 g) was obtained. The product was distilled using a Widmer distillation apparatus to obtain 52 g of 2-pentylidenecyclopentanone (boiling point: 92°C/533 Pa).

Reference Example 5

Synthesis of 2-hexylidenecyclopentanone

35 **[0088]** In a 300 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-(1-hydroxyhexyl)cyclopentanone (85 g) synthesized in Reference Example 2, oxalic acid (1.0 g) and toluene (150 ml), and the whole was refluxed to allow dehydration to proceed. The formed water was removed and the reaction was continued until water was not formed any more (about 3 hours). The reaction mixture was washed with water and the layers were separated from each other. Further, the resulting organic layer was washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover toluene and unreacted cyclopentanone, whereby a crude product (78 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 67 g of 2-hexylidenecyclopentanone (boiling point: 92°C/533 Pa; GC purity: 98.5%).

Reference Example 6

Synthesis of 2-heptylidenecyclopentanone

45 **[0089]** In a 300 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-(1-hydroxyheptyl)cyclopentanone (70 g) synthesized in Reference Example 3, oxalic acid (0.7 g) and toluene (140 ml), and the whole was refluxed to allow dehydration to proceed. The formed water was removed and the reaction was continued until water was not formed any more (about 2.5 hours). The reaction mixture was washed with water and the layers were separated from each other. Further, the resulting organic layer was washed with saturated brine and separated. 50 The organic layer was evaporated on a rotary evaporator under reduced pressure to recover toluene and unreacted cyclopentanone, whereby a crude product (63 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 55 g of 2-heptylidenecyclopentanone (boiling point: 56°C/400 Pa; GC purity: 98.5%). MS (m/e): 180 (M⁺, 22), 123 (64), 110 (18), 97 (100), 84 (49), 67 (18), 54 (16), 43 (11).

Example 1

Synthesis of 2-pentyl-2-cyclopentenone

[0090] In a 100 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-(1-hydroxypentyl)cyclopentanone (20 g) synthesized in Reference Example 1, iodine (0.01 g) and xylene (10 ml), and water was removed under refluxing, followed by 2 hours of the reaction at 170°C. The reaction mixture was washed with water and the layers were separated from each other. Further, the resulting organic layer was washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover xylene, whereby a crude product (19.8 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 17.4 g of 2-pentyl-2-cyclopentenone (boiling point: 105°C/933 Pa; GC purity: 98.2%).

Example 2

Synthesis of 2-pentyl-2-cyclopentenone

[0091] In a 50 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-(1-hydroxypentyl)cyclopentanone (20 g) synthesized in Reference Example 1, N-iodosuccinimide (0.1 g) and toluene (10 ml), and water was removed under refluxing, followed by 4 hours of the reaction at 150°C. The reaction mixture was washed with water and the layers were separated from each other. Further, the resulting organic layer was washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover toluene, whereby a crude product was obtained. The product was distilled using a Claisen distillation apparatus to obtain 15.3 g of 2-pentyl-2-cyclopentenone (boiling point: 104°C/930 Pa; GC purity: 98.4%).

Example 3

Synthesis of 2-heptyl-2-cyclopentenone

[0092] In a 100 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-(1-hydroxyheptyl)cyclopentanone (40 g) synthesized in Reference Example 3, bromine (0.4 g) and n-octane (10 ml), and water was removed under refluxing, followed by 4 hours of the reaction at 120°C. The reaction mixture was washed with water and the layers were separated from each other. The resulting organic layer was washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover n-octane, whereby a crude product (39 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 32 g of 2-heptyl-2-cyclopentenone (boiling point: 111°C/900 Pa; GC purity: 97.8%).

Example 4

Synthesis of 2-hexyl-2-cyclopentenone

[0093] In a 30 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-(1-hydroxyhexyl)cyclopentanone (20 g) synthesized in Reference Example 2 and iodine (5 mg), followed by 6 hours of the reaction at 150°C. The crude product was purified by column chromatography (hexane/ethyl acetate: 95/5) to obtain 15.3 g of 2-hexyl-2-cyclopentenone (GC purity: 99.1%).

Example 5

Synthesis of 2-hexyl-2-cyclopentenone

[0094] In a 50 ml three-neck flask fitted with a thermometer, a condenser and a stirrer were placed 2-hexylidenecyclopentanone (15 g) synthesized in Reference Example 5 and bromine (0.03 g), followed by 6 hours of the reaction at 100 - 120°C. The crude product was purified by column chromatography (hexane/ethyl acetate: 95/5) to obtain 12.5 g of 2-hexyl-2-cyclopentenone (GC purity: 98.5%).

Example 6

Synthesis of 2-pentyl-2-cyclopentenone

[0095] In a 100 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-pentylidenecyclopentanone (30 g) synthesized in Reference Example 4, cyclopentanone (31.6 ml) and iodine (30 mg), followed by 4 hours of the reaction under refluxing. The reaction mixture was washed with water and the layers were separated from each other. The resulting organic layer was washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover cyclopentanone, whereby a crude product (30.2 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 25.3 g of 2-pentyl-2-cyclopentenone (boiling point: 101°C/900 Pa; GC purity: 97.9%).

Example 7

Synthesis of 2-heptyl-2-cyclopentenone

[0096] In a 100 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-heptylidenecyclopentanone (20 g) synthesized in Reference Example 6, bromine (0.05 g) and tetrachloroethylene (10 ml), followed by 4 hours of the reaction under refluxing. The reaction mixture was washed with water and the layers were separated from each other. Further, the resulting organic layer was washed with saturated brine and separated. The organic layer was evaporated on a rotary evaporator under reduced pressure to recover tetrachloroethylene, whereby a crude product (19 g) was obtained. The product was distilled using a Claisen distillation apparatus to obtain 16.8 g of 2-heptyl-2-cyclopentenone (boiling point: 111°C/900 Pa; GC purity: 97.3%).

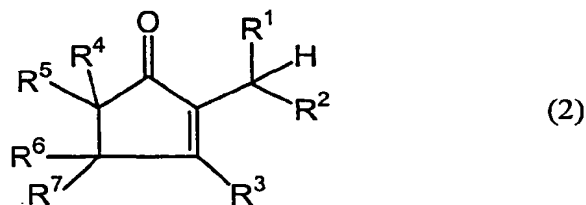
Example 8

Synthesis of 2-pentyl-2-cyclopentenone

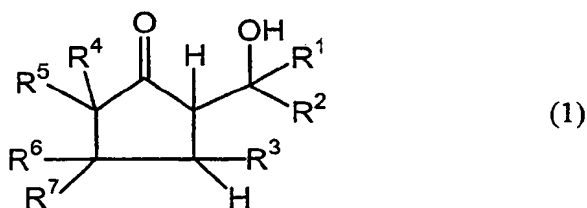
[0097] In a 100 ml four-neck flask fitted with a thermometer, a reflux condenser and a stirrer were placed 2-pentylidenecyclopentanone (50 g) synthesized in Reference Example 4 and iodine (5 mg), followed by 3 hours of the reaction at 180°C. The crude product (50 g) was distilled without any treatment using a Claisen distillation apparatus to obtain 39 g of 2-pentyl-2-cyclopentenone (boiling point: 105°C/933 Pa; GC purity: 98.3%).

Claims

1. A process for producing a 2-alkyl-2-cyclopentenone represented by the following general formula (2):

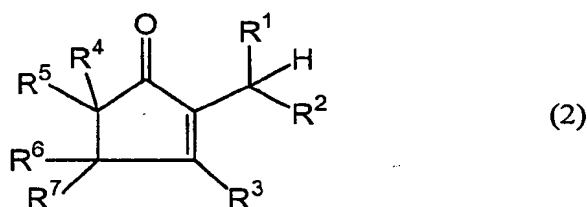


(wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ may be together combined to form a ring which may have a double bond), which comprises a step of dehydrative isomerization of a 2-(1-hydroxyalkyl)cyclopentanone represented by the following general formula (1):

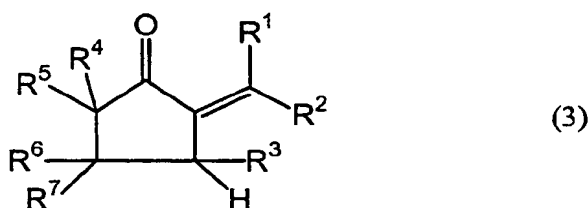


(wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are the same as above) in the presence of a bromine compound and/or an iodine compound.

2. A process for producing a 2-alkyl-2-cyclopentenone represented by the following general formula (2):



(wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ each independently represents hydrogen atom, an alkyl group having 1 to 10 carbon atoms which may have one or more substituents or an aromatic group which may have one or more substituents, and each of (1) R⁶ or R⁷ with R³ and (2) R⁶ or R⁷ with R⁴ or R⁵ may be together combined to form a ring which may have a double bond), which comprises a step of isomerization of a 2-alkylidenecyclopentanone represented by the following general formula (3):



(wherein R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ are the same as above) in the presence of a bromine compound and/or an iodine compound.

3. The process for producing a 2-alkyl-2-cyclopentenone according to claim 1 or 2, wherein R¹ in the general formula (1) or (3) is hydrogen atom.
4. The process for producing a 2-alkyl-2-cyclopentenone according to any one of claims 1 to 3, wherein R³, R⁴, R⁵, R⁶ and R⁷ in the general formula (1) or (3) are each hydrogen atom.
5. The process for producing a 2-alkyl-2-cyclopentenone according to any one of claims 1 to 4, wherein, in the general formula (1) or (3), R² is a linear or branched alkyl group having 2 to 8 carbon atoms which may have one or more unsaturated bonds.
6. The process for producing a 2-alkyl-2-cyclopentenone according to any one of claims 1 to 5, wherein the amount

EP 1 316 541 A1

of the bromine compound or iodine compound is from 0.0001 to 2.0% by weight in terms of bromine or iodine relative to the starting material.

5

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 29 2899

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 033 604 A (INT FLAVORS & FRAGRANCES INC) 12 August 1981 (1981-08-12)	1-6	C07C45/66
X	* page 25, line 30; examples IIB,VIB *	1,3-6	C07C45/67
X	* page 25, line 3; examples IB,IIB,VB,VIB *	2-6	C07C49/597
D,X	& US 4 310 701 A (...) 12 January 1982 (1982-01-12)	1-6	
X	EP 1 134 210 A (KAO CORP) 19 September 2001 (2001-09-19)	1-6	
X	* column 5, line 35 *	1,3-6	
X	* column 4, line 10 *	2-6	
X,D	DATABASE WPI Section Ch, Week 199320 Derwent Publications Ltd., London, GB; Class B05, AN 1993-162105 XP002169658 & JP 05 092934 A (NIPPON ZEON KK), 16 April 1993 (1993-04-16) * abstract *	1,3-6	
X	DATABASE WPI Section Ch, Week 199416 Derwent Publications Ltd., London, GB; Class B05, AN 1994-131993 XP002169659 & JP 06 080606 A (KAO CORP), 22 March 1994 (1994-03-22) * abstract *	2-6	C07C
X	DD 154 604 B (SCHMIDT RENNER WOLFGANG;ALDER ERNST; KRAUS WALTRAUT; KUEBLER RENATE; M) 7 April 1982 (1982-04-07) * the whole document *	2-6	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 12 March 2003	Examiner Janus, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/02 (P4C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 29 2899

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-03-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0033604	A	12-08-1981	US 4260830 A	07-04-1981
			US 4310701 A	12-01-1982
			DE 3160570 D1	18-08-1983
			EP 0033604 A1	12-08-1981
			JP 1582791 C	22-10-1990
			JP 2009567 B	02-03-1990
			JP 56147740 A	16-11-1981

EP 1134210	A	19-09-2001	EP 1134210 A1	19-09-2001
			JP 2001328965 A	27-11-2001
			US 2001049455 A1	06-12-2001

JP 5092934	A	16-04-1993	NONE	

JP 6080606	A	22-03-1994	JP 3241814 B2	25-12-2001

DD 154604	B	07-04-1982	DD 154604 A1	07-04-1982

EPO FORM P/0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82